

# Synthesis and properties of novel phenylethynyl-containing organodisulfide as cathode material for secondary lithium batteries

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**Abstract** A novel phenylethynyl-containing conjugative organodisulfide compound 9-trimethylsilane ethynyl-5,8-dihydro-1*H*,4*H*-2,3,6,7-tetrathia-anthracene (TMSEDTTA) was synthesized by a facile preparation method, characterized by elemental analysis, Fourier transform infrared spectroscopy (FT-IR), Raman spectrum, X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA), and was tested as cathode active material in rechargeable lithium batteries. The electrochemical properties of S–S bonds redox behavior in the organodisulfides were investigated in 1.0 M LiClO<sub>4</sub>/EC/DMC (1:1, v/v) solution. The system has many advantages, such as high theoretical charge density (ca. 365 mAh g<sup>−1</sup>), fast redox process and enhanced reversibility. The fast redox process and enhanced reversibility are due to the intramolecular cleavage-recombination of the S–S bond, and the intramolecular electrocatalytic effect of phenylethynyl chain. The cyclic voltammogram of TMSEDTTA shows multiple redox peaks. The separation of the anodic and cathodic peak potentials for disulfide bond in TMSEDTTA is 0.4 V. The charge–discharge tests show an initial capacity of 330 mAh g<sup>−1</sup> and the coulomb efficiency of more than 80 % after the electrochemical activation.

**Keywords** Secondary lithium batteries · Organodisulfide · Cathode material · Synthesis · Electrochemical properties

## 1 Introduction

The development of lightweight and high energy density rechargeable batteries is of importance with the increasing demand for mobile power and the extensive use of portable devices [1]. Elemental sulfur has the highest specific capacity (1,672 mAh g<sup>−1</sup>) and lowest cost among all the known cathode material candidates, but the self-discharge and insulating nature make it unable to be employed in applied lithium batteries [2, 3]. Since Visco and coauthors [4, 5] found organic disulfide compounds could be used as cathode active materials for rechargeable lithium battery in the late of 1980s, many researchers have focused on the development of organic disulfides materials [6–13]. Recently, a series of organodisulfide polymers having S–S group in molecule have been put forward in the field [14–17]. These disulfide compounds have electrochemical interest due to redox reaction ( $\text{RS-SR} + 2\text{e}^- = 2\text{RS}^-$ ) [18, 19]. They also have much higher theoretical capacity than that of conventional cathode materials for lithium battery, such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, and LiMn<sub>2</sub>O<sub>4</sub>. The most noteworthy character of them is that the S–S bond is linked to the main-chain of a conducting polymer, the modification in the structure not only enable the catalytic effect of the backbone chain on the redox process of disulfides, it also bring about an effective inhibition of the loss of sulfur in the electrolyte during the charge and discharge. At the same time, polyphenylacetylene as one of the most promising intrinsically conducting polymers due to its straightforward polymerization, chemical and environmental stability, and relatively high conductivity, has been widely studied for the applications of electronic and optical devices [20–23]. It is noted that the acetenyl group attached to the main-chain is coplanar to the phenyl ring, facilitating the electric charge transfer. With this in mind, we designed

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novel conjugative compound with sulfide side-chains to accept or donate electrons and phenylacetylene as main chain to offer good electronic conductivity. In this paper, 9-trimethylsilane ethynyl-5,8-dihydro-1*H*,4*H*-2,3,6,7-tetra-thia-anthracene (TMSEDTTA) was synthesized, characterized, and tested as cathode materials; the structure of the compound and synthetic route are depicted in Fig. 1; the electrochemical properties and energy storage abilities are described *vide infra*. The charge–discharge tests exhibited that TMSEDTTA was electrochemically active as a cathode material in rechargeable batteries, which provides potential for a new field of rechargeable organic cathode materials.

## 2 Experimental

### 2.1 Apparatus and procedures

FT-IR spectra and Raman measurements were recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets and a NEXUS670 spectrophotometer, respectively. XPS test was carried out on a KRATOS XSAM800 instrument with the magnesium source Mg K $\alpha$  1253.6 eV operated at 12.5 kV and 16 mA. Elemental analysis was determined using a Vario EL III CHNS elemental analyzer. The NMR spectra were recorded on a Varian Mercury-VX 300 spectrometer. Chemical shifts were given as  $\delta$  values against tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a Thermo Finnigan TRACE MS PLUS (EI) instrument. Thermal analysis was performed on a Diamond DSC TG–DTA 6300 instrument under nitrogen flow at a heating rate of 10 °C min<sup>−1</sup>. Cyclic voltammetry

(CV) tests were carried out on an electrochemical workstation (CHI660) at a scan rate of 0.1 mV s<sup>−1</sup> between 1.4 and 4.4 V. The charge–discharge tests were performed on a Land Battery Test System at a current density of 32.6 mA g<sup>−1</sup>. The lithium batteries were fabricated with the composite containing TMSEDTTA (40 wt%), acetylene carbon (40 wt%) and poly(tetrafluoroethylene) (20 wt%) as the cathode, 1.0 M LiClO<sub>4</sub>/EC/DMC (1:1, v/v) solution as the electrolyte and lithium foil used as the anode.

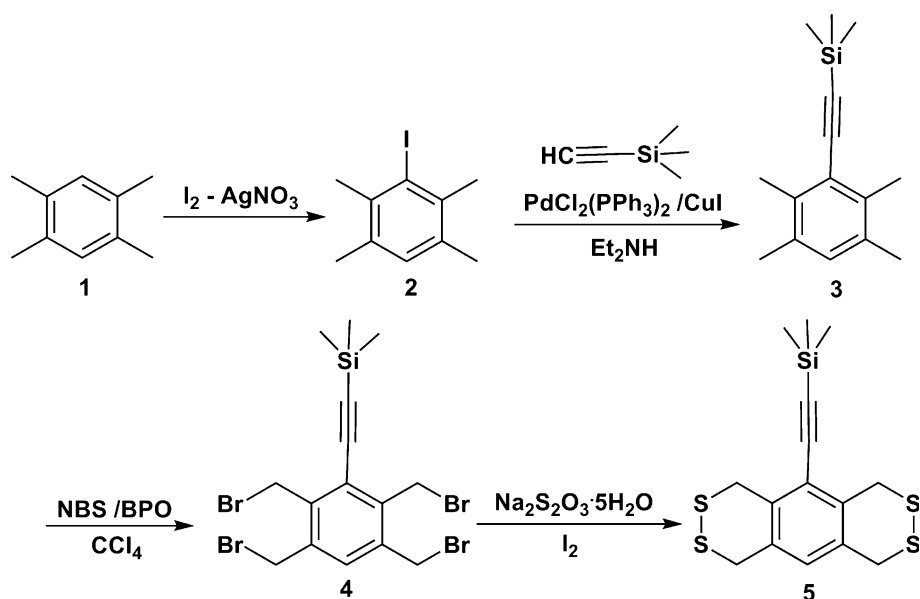
### 2.2 Synthesis of TMSEDTTA

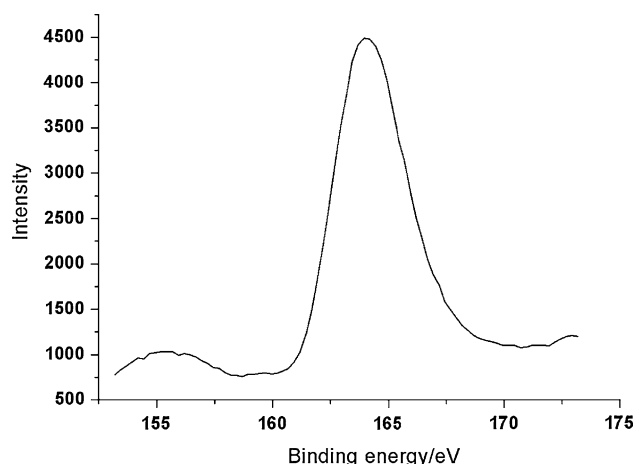
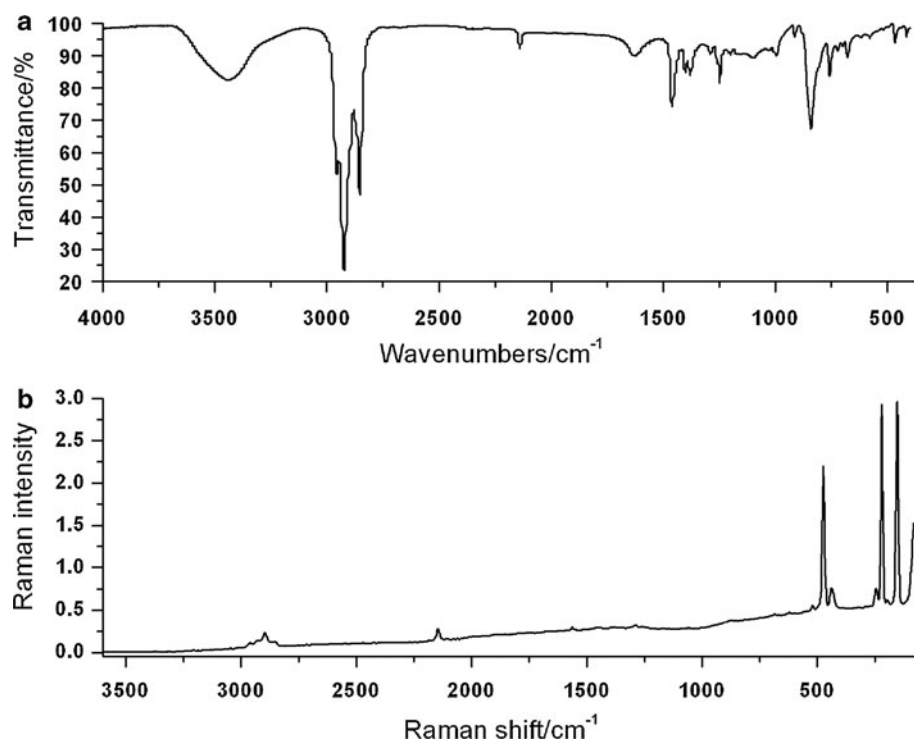
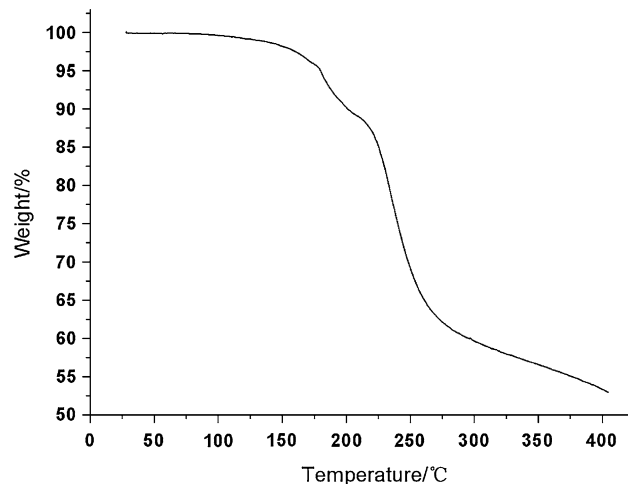
The synthesis for target compound TMSEDTTA was achieved in four steps starting from 1,2,4,5-tetramethylbenzene (**1**) as outlined in Fig. 1. The compounds **2** and **3** were prepared via similar methods described as the literatures [24, 25]. All other chemicals were of reagent grade and used directly as received unless otherwise mentioned.

#### 2.2.1 Synthesis of compound **4**

To a round bottom Schlenk flask containing **3** (2.82 g, 12.3 mmol), benzoyl peroxide (0.61 g, 2.4 mmol) and CCl<sub>4</sub> (90 mL) was alternately added *N*-bromosuccinimide (15.74 g, 88.4 mmol) in small portions under nitrogen protection. The mixture was stirred at mild reflux for 12 h. After filtration of succinimide and removal of solvent, the residue was purified by column chromatography (petroleum ether as eluant). And the resulting solid (*R*<sub>f</sub> = 0.3) was recrystallized from petroleum ether to give pure **4** as white solid (30 %). mp: 128–129 °C <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (s, 1H), 4.86 (s, 4H), 4.57

**Fig. 1** The synthetic route of TMSEDTTA



**Fig. 2** FT-IR and Raman spectra of TMSDDTA**Fig. 3** XPS spectrum of TMSDDTA**Fig. 4** TGA curve of TMSDDTA

(s, 4H), 0.34 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.4, 137.6, 132.8, 126.3, 108.3, 98.2, 28.9, 27.2,  $-0.38$ . GC-MS (EI,  $m/z$ ): 546( $\text{M}^+$ , 100).

### 2.2.2 Synthesis of compound **5** (TMSDDTA)

The compound **4** (1.67 g, 3.06 mmol) and sodium thiosulphate (3.34 g, 13.5 mmol) were dissolved in 30 mL of anhydrous  $\text{EtOH}/\text{H}_2\text{O}$  (1:1, v/v). The mixture was refluxed with stirring until the solution was homogeneous. Iodine (1.61 g, 6.34 mmol) was then added in small portions until the color remained. Next, a sodium bisulfite

solution was added to remove the excess iodine. After filtration, the brown precipitation was washed with water and dried in vacuum at 60 °C and then extracted by 100 mL of boiling  $\text{CHCl}_3$ . Evaporation of solvent left the crude product, which was purified using silica gel chromatography (PE/chloroform 3: 0.2) to give 0.20 g (total yield 20 %) of **5** as a white solid. mp: 175–176 °C  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.80 (s, 1H), 4.16 (s, 4H), 3.99 (s, 4H), 0.28 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 131.7, 131.1, 124.5, 108.7, 99.6, 34.9, 32.6,  $-0.04$ . FT-IR (KBr) 758, 678 ( $\nu_{\text{C-S}}$ )  $\text{cm}^{-1}$ . FT-Raman 521

( $\nu_{S-S}$ )  $\text{cm}^{-1}$ . Elem. Anal. Calc. for  $\text{C}_{15}\text{H}_{18}\text{S}_4\text{Si}$  (%): C, 50.80; H, 5.12; S, 36.17; Found (%): C, 50.84; H, 5.06; S, 36.50. ESI HRMS for  $\text{C}_{15}\text{H}_{18}\text{S}_4\text{Si}$   $[\text{M} + \text{H}]^+$ : Found 352.9989, Calc. 352.9977.

### 3 Results and discussion

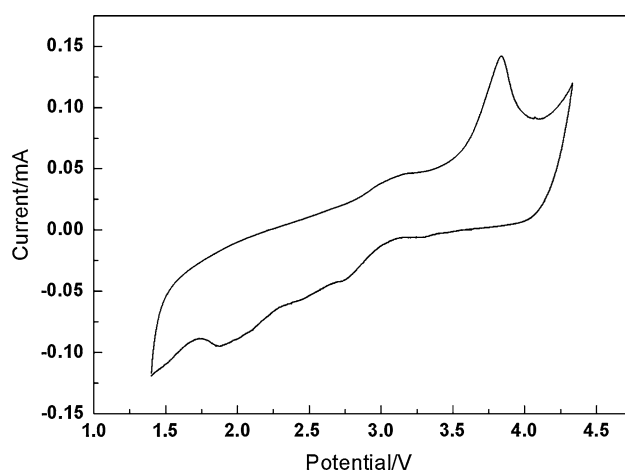
#### 3.1 Materials and characterization

The structure of TMSEDTTA has been characterized by FT-IR, Raman, XPS, and TGA. In Fig. 2a, the FT-IR spectrum shows a band around  $2,140\text{ cm}^{-1}$ , which is ascribed to the  $\text{C}\equiv\text{C}$  stretching vibration. The presence of C–S bond is supported by the absorption peaks at 758 and  $678\text{ cm}^{-1}$  ( $\nu_{\text{C-S}}$ ). The bands at  $2,924\text{--}2,853\text{ cm}^{-1}$  originated from the  $\text{CH}_2$  two pairs of bending vibration. Sulfur-rich compounds give very intense Raman spectra since the valence electrons in S–S bonds are highly polarizable. Therefore, Raman analysis (Fig. 2b) has been carried out to confirm the formation of S–S bond. The peak at  $521\text{ cm}^{-1}$  in Raman spectrum is assigned to the stretching band of S–S in TMSEDTTA. The XPS spectrum of TMSEDTTA (Fig. 3) is also examined. The binding energy of S2p is located 163.7 eV and shows that sulfur in TMSEDTTA has only one valence state. Thermal gravimetric analysis (TGA, Fig. 4) demonstrates a high thermo-stability, which reveals that the obtained TMSEDTTA is stable up to about  $180^\circ\text{C}$  (5 % weight loss). Major decomposition occurs in the region between 200 and  $300^\circ\text{C}$ .

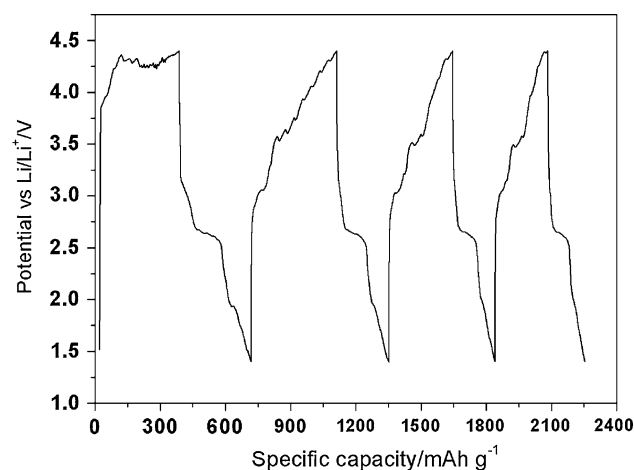
#### 3.2 Electrochemical behavior

##### 3.2.1 The cyclic voltammetry test results

Cyclic voltammogram for TMSEDTTA adhered on Al foil in 1.0 M  $\text{LiClO}_4/\text{EC}/\text{DMC}$  (1:1, v/v) is presented in Fig. 5, and exhibits two oxidative peaks. One peak locates at 2.8–3.3 V with a maximum value at 3.0 V, while the other peak locates at 3.5–4.1 V with a maximum value at 3.8 V. The high oxidative peak indicates that the monomer may be charged at high voltage as cathode material. Meanwhile the reductive peaks are well defined with two bands at 1.8–2.0 V and 2.6–2.9 V. The broad oxidation and reduction peaks may result from the overlap of close peaks of multi-step process of the redox reaction. A reduction peak at ca. 2.6 V is the cleavage of the S–S bond and an oxidation peak at ca. 3.0 V is the reformation of the disulfide group. These cyclic voltammograms can be used for qualitative assessment of the kinetic reversibility of the redox couples in TMSEDTTA. And it is well known that kinetic reversibility is an important parameter for energy storage application. At a given sweep rate, the smaller the



**Fig. 5** Cyclic voltammogram of TMSEDTTA adhered on Al foil in 1.0 M  $\text{LiClO}_4/\text{EC}/\text{DMC}$  (1:1, v/v) at room temperature, scan rate:  $0.1\text{ mV s}^{-1}$

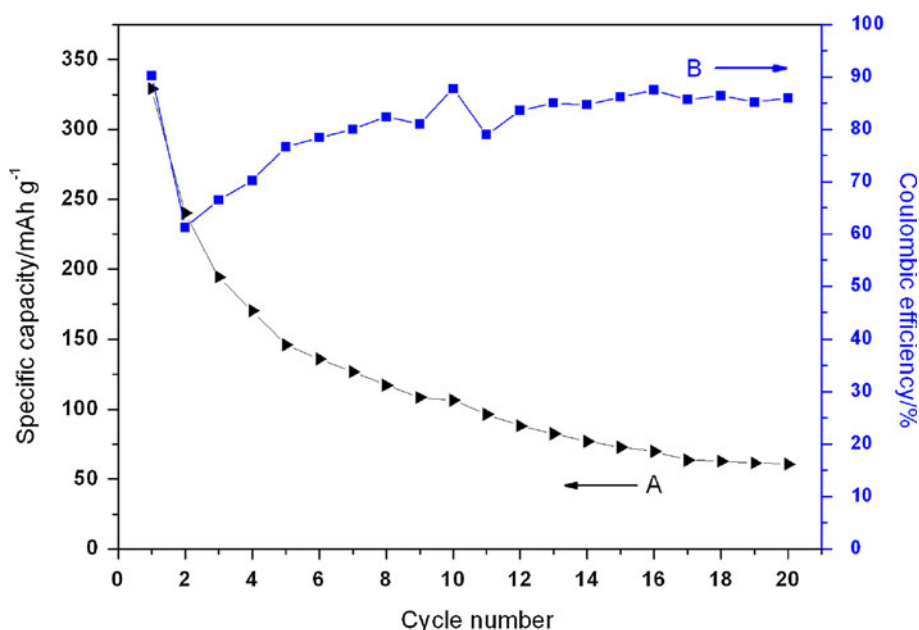


**Fig. 6** The first four cycles of charge–discharge curves for TMSEDTTA cathode (TMSEDTTA/acetylene carbon/PTFE: 1:1:0.5 wt/wt) in 1.0 M  $\text{LiClO}_4/\text{EC}/\text{DMC}$  (1:1, v/v). Current density:  $32.6\text{ mA g}^{-1}$ ; cutoff voltage: 1.4–4.4 V

separation of the anodic and cathodic peak potentials, the faster the electrode kinetics of redox pairs in organodisulfide. Here, the potential peak gap of the redox of S–S bond for TMSEDTTA is 0.4 V, which is smaller than that of the reported disulfide compounds [17]. The results show that redox couple of TMSEDTTA can be reversible.

##### 3.2.2 The charge–discharge experimental results

The charge–discharge test for a lithium battery with TMSEDTTA as cathode material was performed with a current density of  $32.6\text{ mA g}^{-1}$  at the potential range from 1.4 to 4.4 V. Figure 6 shows the first four charge–discharge cycles of TMSEDTTA electrode. After the first charging for activation that might be attributed to the electrochemical



**Fig. 7** The specific capacity and coulomb efficiency of TMSEDTTA cathode (TMSEDTTA/acetylene carbon/PTFE: 1:1:0.5 wt/wt) in 1.0 M LiClO<sub>4</sub>/EC/DMC (1:1, v/v). Current density: 32.6 mA g<sup>-1</sup>; cutoff voltage: 1.4–4.4 V

polymerization of unit phenylethynyl existed in TMSEDTTA, a pair of main charging and discharging plateaus appears at ca. 3.0 and 2.6 V, respectively. It can be seen that the charge voltage and discharge voltage correspond roughly to the oxidation and reduction potentials in the CV test, as shown in Fig. 5. The maximal discharge capacity of the cathode active material is 330 mAh g<sup>-1</sup>, which should include both contributions of phenylethynyl and S–S bonds in TMSEDTTA. On the other hand, the charge–discharge voltages are similar to the previously reported disulfide containing cathode materials [9, 10]. Obviously, the displayed multi-plateaus and discharge voltage are the characteristic of disulfide compounds in lithium batteries and mainly attributed to the redox reaction of disulfide bonds.

The cycling-specific capacity and coulomb efficiency of TMSEDTTA versus cycle numbers are shown in Fig. 7. The specific capacity of TMSEDTTA reached 330 mAh g<sup>-1</sup> at the first cycle but decreased dramatically to only 70 mAh g<sup>-1</sup> at the 20th cycle, indicating a rapid escape of the monomer from the cathode during the charge–discharge process. The coulomb efficiency of TMSEDTTA is more than 80 % after the 5th cycle, which can be ascribed to the intramolecular catalysis and its special structure. That is to say, the electrochemical cleavage and recombination process of S–S bond is enhanced very much by the phenylethynyl main chain, which is similar to the electrocatalytic effect that has been observed in polyaniline/DMcT [26]. To improve the charge–discharge stability and increase the coulomb efficiency of TMSEDTTA-containing material, polymerization of the TMSEDTTA should be conducted.

The corresponding research work on polymerization is under way.

#### 4 Conclusions

A new cathode material, TMSEDTTA, has been successfully synthesized for secondary lithium batteries. The enhanced redox properties of TMSEDTTA were confirmed by the cyclic voltammetry. The separation of the anodic and cathodic peak potentials, that corresponding with the electrochemical cleavage and recombination process of S–S bond for TMSEDTTA is 0.4 V. The discharging tests of Li/TMSEDTTA cell show a maximal discharge capacity of 330 mAh g<sup>-1</sup> with a plateau at ca. 2.6 V. The charge efficiency is more than 80 % after activation, indicating an improved reversibility. We expect that further improvements to the capacity and cyclability will make organosulfur compounds potential cathode materials for rechargeable lithium batteries.

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